

Precise Measurements With Bingham Viscometers and Cannon Master Viscometers.

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A critical study has been made of the techniques used at the National Bureau of Standards with Bingham viscometers and Cannon kinematic viscometers. All corrections applicable to measurements with these instruments were critically examined. Instruments of each type were calibrated using the viscosity of water at 20° C as the primary viscosity standard. The viscometers were used to determine the viscosities of four hydrocarbon liquids in the range 0.4 to 40 centipoises. With each liquid, the values obtained in the two types of viscometers were in agreement by 0.05 percent or better, indicating that no gross error was involved in the use of either instrument. It is considered, however, that the inherent relative simplicity of operation of the kinematic viscometer makes it a preferable instrument for this type of measurement.

1. Introduction

As the result of a recent determination [1]¹, the National Bureau of Standards on July 1, 1953, adopted the value of 1.002 centipoises (cp) for the absolute viscosity of water at 20° C as the primary standard for viscosity determinations. The American Society for Testing Materials, The National Physical Laboratory in England, and the Physikalisch-Technischen Bundesanstalt in Germany have concurred in this action. Previous to this, the values of the secondary standards of viscosity issued by the Bureau were based upon 1.005 cp for the viscosity of water at 20° C. In connection with the reevaluation of the secondary standards on the basis of the new value for water, a comparative study has been made of the use of two types of viscometers for relating the viscosities of other liquids to that of water as a primary standard. Bingham viscometers and Cannon viscometers were used, and comparisons were made of the viscosities of four hydrocarbon liquids in the range 0.4 to 40 cp and of the viscosity of each liquid as determined in each type of instrument. This paper presents in some detail the techniques used in making these determinations to describe the methods employed in evaluating the National Bureau of Standards standard viscosity samples and to call attention to the magnitude of certain corrections often neglected in viscometry. The extension of these techniques to the calibration of viscometers with larger capillaries suitable for the measurement of the viscosities of more viscous liquids is relatively simple and involves the same methods as are covered here.

2. The Bingham Viscometer

2.1. General

A short treatment of the use of the Bingham viscometer, shown diagrammatically in figure 1, has been given previously [2], and it will be assumed that

¹ Figures in brackets indicate the literature references at the end of this paper.

the reader has some familiarity with the instrument. With the usual procedure, pressure is applied to the right limb of the viscometer, and the rate of flow is determined by measuring the time required for the meniscus in the left limb to pass from the fiducial mark d to mark c. To avoid the necessity for drainage corrections, each determination is made with the bulb A initially dry. This is accomplished by introducing the sample into bulb B with a special pipet, sufficient liquid being added to fill the viscometer between the marks d and g at the test temperature. With the exception of certain calibration runs with water, the viscometer is cleaned and a fresh sample is introduced for each measurement. By this procedure the volume of flow is kept constant for each instrument regardless of the viscosity or rate of flow.

Pressure is applied to the liquid in the viscometer by air supplied from a tank having a capacity (about 60,000 cm³) sufficiently large that the increase in volume (about 4 cm³) in the pressure system during the flow of liquid from bulb B causes no significant reduction in pressure. The tank is thermally insulated to prevent rapid changes in its temperature

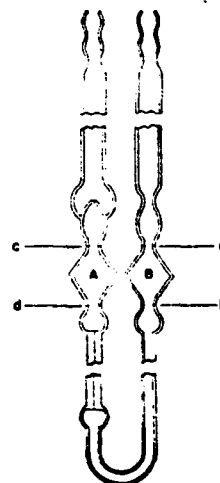


FIGURE 1. Bingham viscometer.

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with fluctuations in the ambient temperature. In general, pressures above 150 mm Hg are read with a mercury manometer, a water manometer being used for lower pressures; differences in liquid levels in the manometer up to 600 mm are read with a cathetometer and greater differences are read by using a calibrated steel tape and reading telescopes. The heights were read to about 0.02 mm with the cathetometer and 0.1 mm with the steel tape.

Times of flow are measured using a stopclock operated from a constant-frequency source of power.

All of the flow measurements reported here were made with the viscometers immersed in a well-stirred, 30-gal oil bath whose temperature was controlled by supplying a heater from the output of a manually adjusted variable transformer. When operating below ambient temperature, heat was taken from the bath through cooling coils in which cold water was circulated at a constant rate. Temperatures were measured with a resistance thermometer, and their recorded values are believed to be accurate to $\pm 0.002^\circ \text{C}$.

2.2. Calibration

The usual form of the modified Poiseuille equation for the calculation of viscosity by the capillary method is

$$\eta = \frac{\pi r^4 P t}{8 V (l + n r)} - \frac{m \rho V}{8 \pi (l + n r) t} \quad (1)$$

where

- r = radius of capillary
- P = mean effective pressure drop through the capillary
- V = volume between fiducial marks
- t = time for volume V to flow
- l = length of capillary
- m, n = coefficients associated with the flow at the ends of the capillary
- η, ρ = the absolute viscosity and density of the liquid whose viscosity is to be determined;

As over a considerable range of rates of flow, m and n can be taken as constant for capillaries having square-cut ends [3], certain of the quantities in eq (1) are usually grouped to give two constants for the instrument. Equation (1) then takes the form

$$\eta = C P t - C' \rho / t, \quad (2)$$

where

$$C = \frac{\pi r^4}{8 V (l + n r)} \text{ and } C' = \frac{m V}{8 \pi (l + n r)}.$$

With viscometers having capillary bores small enough for calibration with water, these two constants are commonly evaluated by measuring the times of flow of water at 20°C for various applied pressures. The product Pt is plotted against $1/t$, and C and C'

are evaluated from the resulting straight line by introducing known values for η and ρ . For the two water-calibrated viscometers used in the work reported here, however, it was found that such plots did not yield straight lines over the complete range of rates of flow in which the instruments were to be used, indicating that m and n were both varying, and consequently C and C' could not be treated as constants. For this reason and for simplicity, the purely empirical formula,

$$\eta = f P t, \quad (3)$$

was used with the viscometers. In this equation, f is a multiplying factor that varies with the conditions of flow. It is convenient to assume that the conditions peculiar to a given rate of flow are characterized by the corresponding value of the Reynolds number as calculated for the flow in the capillary ($R = 2 V \rho / \pi r \eta t$), and therefore f will have a definite value for each value of the Reynolds number. The calibration of these instruments, then, consists of determining the value of f as a function of the Reynolds number.

Although the Bingham viscometer is designed to minimize the effect of hydrostatic head in the instrument, actually small head corrections to an applied external pressure, p_0 , are necessary to give an exact value of P . The first correction, which will be called the level head, arises from the fact that, despite careful construction, the two bulbs (A and B in fig. 1) will not be geometrically identical and at the same level. This condition results in a residual hydrostatic head that is of the same magnitude but opposite sign for flow right to left (R-L) and left to right (L-R) in the viscometer. The correction is largely independent of the magnitude of the applied external pressure but is proportional to the density of the liquid. The level head was evaluated in this work by making flow measurements in the L-R direction and then repeating in the R-L direction, using approximately the same applied pressure. The runs were made at the lowest applied pressure that could be accurately measured, and under conditions chosen to insure that the volume of flow was the same in each direction. Under these conditions, the difference in the time of flow for the two directions was attributed to a corresponding difference in pressure. Then, knowing the applied pressures, the magnitude of the correction was calculated.

A second head correction, which becomes very significant at low values of the applied pressure, is the commonly termed logarithmic head correction. If we neglect for the moment the level head discussed above, the initial pressure drop through the capillary is $p_0 + x$, where x is the initial hydrostatic head of liquid, and the final pressure is $p_0 - x$, but the mean effective pressure is not exactly p_0 , the arithmetic mean of the two, since the higher pressures during the first part of the run cause more rapid flow and are therefore effective for a proportionately shorter

time. For bulbs of regular shape, however, the effective pressure is readily calculable. For this work, the calculations were made by using Barr's equation [4]. This equation is written $P(1+y^2/10+y^4/35+\dots)=p_0$, [approximately, where $y=r/p_0$. Barr states that this equation is derived "for a bulb that has the form of a pair of opposed cones, each of a height equal to the radius of the common base, discharging into air, or for such a bulb discharging symmetrically into a similar one, as in Bingham's viscometer". The correctness of this expression was verified in an independent derivation, but because the radius of the common base dropped out in the derivation, it is concluded that the expression holds for cones of any height-to-base ratio. It is of importance to note in connection with runs at low pressures, that the logarithmic head is a function of the ratio of the initial and final pressures, and therefore it increases in absolute magnitude as the applied pressure is reduced. The sign of the correction is always negative, no matter which direction of flow is being used in the viscometer, and therefore it does not affect the determination of the level head, as described above.

The design of the Bingham viscometer is such as to minimize the effect of surface tension upon P . Calculations of the net contribution of surface tension to the mean effective pressure indicate a maximum correction of about 0.001 mm Hg, which was neglected in this work.

A more complete discussion of the above corrections is given by Barr [3, chap. 3].

The three Bingham viscometers used are identified in table 1. Of these, viscometers 1 and 20 were calibrated with water, whereas number 5 was calibrated subsequently by using two hydrocarbon oils whose viscosities were determined in viscometers 1 and 20. In making the calibration runs with water an exception was made to the usual procedure of flowing into a dry bulb, most of the runs being made with the fiducial bulb wet. Following each R-L run, the liquid was drawn back at such a rate as to require about 80 sec with viscometer No. 1, and 120 sec with No. 20 for the fiducial bulb to empty. After allowing about 18 min for further drainage from the walls of the bulb, another R-L run was started. In this manner a reproducible volume of flow was obtained without the necessity of drying the instrument between runs. The difference between the volume of flow under this wet-bulb condition and the true volume of the fiducial bulb was obtained from the differences in the product Pt between wet and

dry-bulb runs made with the same applied pressure. On this basis, all the wet-bulb runs were corrected to dry-bulb conditions.

The calibration data obtained with water at 20° C for viscometers 1 and 20 are given in appendices 7.1 and 7.2. All runs were made in the R-L direction, except for the few special runs made for the determination of the level head corrections. From these data the plots of Pt versus R given in figures 2 and 3 were constructed. Each plotted point represents the mean of at least two runs made at approximately the same pressure. For each viscometer, it is seen that the plot is not linear at certain values of R , as was mentioned previously. Since the data are not adequate to position accurately the curves at the lowest Reynolds numbers, the lines were drawn horizontal in this region on the basis of theoretical considerations [5]. From these curves values of Pt corresponding to selected values of R were obtained and, taking $\eta=0.01002$ poise, were substituted

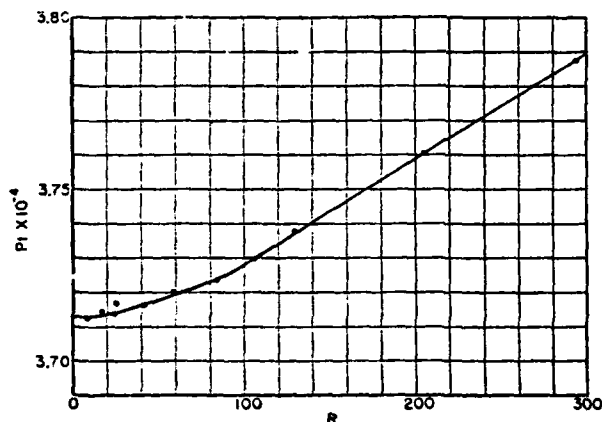


FIGURE 2. Pt as a function of Reynolds number for Bingham viscometer number 1.

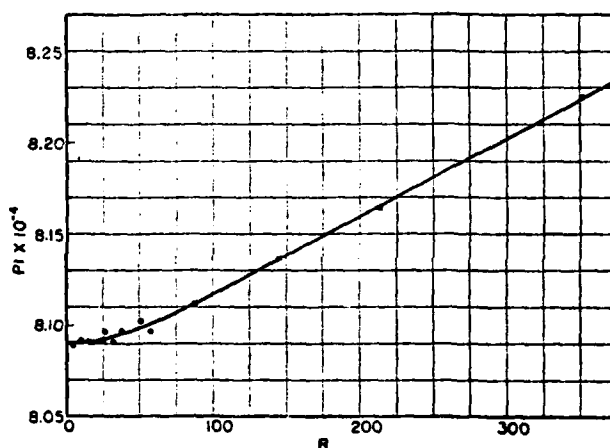


FIGURE 3. Pt as a function of Reynolds number for Bingham viscometer number 20.

TABLE 1. Essential dimensions of Bingham viscometers

Viscometer	Capillary		Volume of flow
	Radius	Length	
1.....	cm 0.012	cm 10.2	cm ³ 3.96
20.....	.011	12.3	3.07
5.....	.017	10.0	4.00

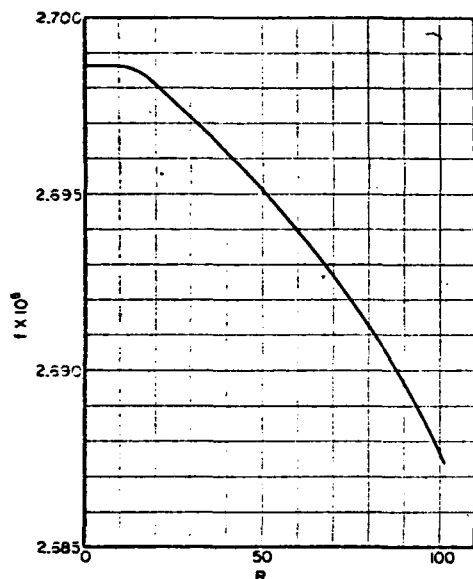


FIGURE 4. Calibration curve for Bingham viscometer number 1.

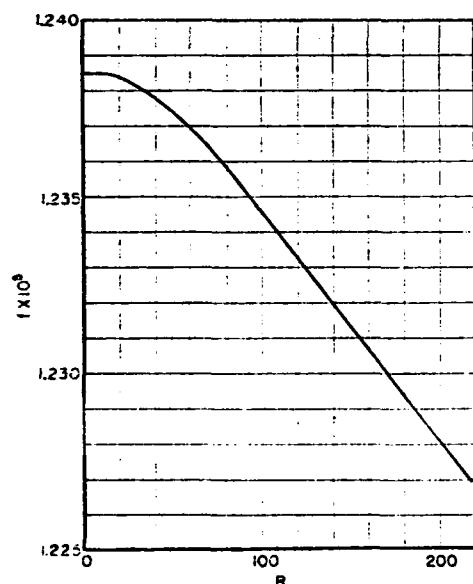


FIGURE 5. Calibration curve for Bingham viscometer number 20.

in eq (3) to calculate corresponding values of f . The values of f were then plotted as a function of R , yielding the calibration curves for viscometers 1 and 20 shown in figures 4 and 5, respectively.

To calculate the unknown viscosity of a liquid from flow data obtained in one of these viscometers, it is necessary to choose a value f from the calibration curve corresponding to a tentative value of the Reynolds number based on an estimate of the viscosity of the unknown. If the viscosity value

calculated by substituting this value of f , together with the measured values of P and t , in eq (3) differs materially from the first estimate of the viscosity, a second calculation is required.

Viscometer No. 5 was calibrated with oils A and B (to be identified later), using values of their viscosities as determined in viscometers 1 and 20. These calibration data are given in appendix 7.3. As all calibrating runs and viscosity measurements made in viscometer 5 were at Reynolds numbers less than 10, it was assumed that f in eq (3) was constant for this viscometer under these conditions. The level head was measured and the logarithmic head calculated for this viscometer as outlined previously.

2.3. Results with Bingham Viscometers

The viscosities of normal heptane and three additive-free hydrocarbon oils were measured at 20° C. The mean results are given in table 2, and

TABLE 2. Results at 20° C with Bingham viscometers

Oil	Visco- meter	R	η	η , mean
n -Heptane	1	98.9	0.4112	0.4111
Do.	20	154.3	0.4110	
A	1	28.2 and 2.4	1.9250	1.9250
A	20	18.1	1.9251	
B	1	2.4	7.609	7.610
B	20	1.5	7.610	
C	5	0.2 and 0.5	42.82	42.82

data from individual runs in appendix 7.4. Normal heptane was included to furnish comparative results with a liquid whose viscosity is less than that of water. The heptane was not of highest purity, but was taken from a lot which met specifications for a primary reference fuel for the determination of octane number [6] and was at least 99.5 percent pure. The viscosities of n -heptane and oils A and B were determined in viscometers 1 and 20, employing the normal procedure of running in the R-L direction with the fiducial bulb initially dry. Oil A was run at as high and as low Reynolds numbers as was practical. Higher applied pressures were avoided because experience has shown that oils as light as A dissolve air rather rapidly under these conditions, with a consequent lowering of their viscosities. Conditions for the other runs were chosen to strike a balance between optimum conditions for accurate measurement of pressure and of time. In calculating the viscosities, small corrections were made to account for the change of viscosity of the oils with pressure. Observed viscosities were reduced to a pressure of 1 atm, as described elsewhere [2], by adding a second term to eq (3), which then becomes

$$\eta = fPt - FP\eta, \quad (4)$$

where F is a factor representing the fractional change in η for unit change in pressure. Good agreement was found between results obtained in the two viscometers 1 and 20, the largest discrepancy being 0.05 percent with *n*-heptane. In addition, results obtained with oil A in viscometer 1 at $R=28.2$ and $R=2.4$ were in equally good agreement (see appendix 7.4), which tends to confirm the shape of the calibration curve at the lower range of Reynolds numbers (fig. 4).

Runs made with oil C in viscometer 5 at high and at low pressures were in good agreement (see appendix 7.4), indicating that the corrections applied for change of viscosity with pressure are not in serious error.

3. The Cannon Viscometer

3.1. General

In outline, the techniques used at the National Bureau of Standards with the Cannon viscometers, shown in figure 6, are substantially as described by Cannon [7], the principal differences consisting of a more rigorous treatment of the various corrections to be applied to the observed data. With instruments of the kinematic type the value of P applicable to eq (1), neglecting surface tension effects, is given by

$$P = hq(\rho - \rho_s), \quad (5)$$

in which h is the mean effective head, ρ is the liquid density, and ρ_a is the mean density of the air column in the left arm of the viscometer, as shown in figure 6. For application to the Master viscometers, eq (1) then becomes

$$\frac{\eta}{\rho} = \frac{\pi r^3 g}{8V(l+nr)} h \left(1 - \frac{\rho_a}{\rho}\right) t - \frac{mV}{8\pi(l+nr)t}. \quad (6)$$

76 W. 124

$$\frac{\pi r^2 g}{8 V (1 - \mu r)} h \left(1 - \frac{\rho_1}{\rho} \right) = K$$

and

$$\frac{mV}{S_{\pi}(l-nr)} = B.$$

eq (6) becomes

$$\frac{\eta}{\rho} = Kt - \frac{B}{t}, \quad (7)$$

It is apparent that K and B will not be constant for all test conditions, but their values will reflect any variations in m and n with Reynolds number. As is done with the Bingham viscometers, these changes in m and n are implicitly determined experimentally as a part of the viscometer calibration. In addition, the value of K changes with any change in h or $1 - \rho_s/\rho$, and a small correction for variation in the value of g may be required if the instrument is used

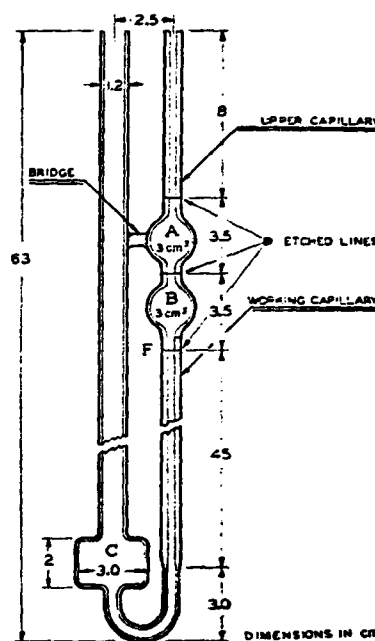


FIGURE 6. Cannon Master viscometer.

at a location other than where it is calibrated. If we let K_z be the determined value of K under the particular hydrostatic head at calibration, we can find from it the value of K under other test conditions by calculating changes in h and $(1-\rho_a/\rho)$. Since a change in $(1-\rho_a/\rho)$ is equivalent to a change in h , it is grouped with the other factors which affect h . For any test condition, eq (7) may then be written

$$\frac{\eta}{\sigma} = K_c \left(1 + \frac{\Delta h}{h} \right) t - \frac{B}{t}, \quad (8)$$

in which Δh is the difference in effective head between test and calibrating conditions, and is made up of the sum of Δh_1 , Δh_2 , etc., arising from the several factors involved. In practice it is convenient to treat K as a constant equal to K_c and to apply the corrections to the time of flow t . The viscosity is calculated by means of the equation

$$\frac{\eta}{\rho} = K_c t_c - \frac{B}{t}, \quad (9)$$

in which $t_c = t(1 + \Delta h/h)$.

Of the factors affecting h , the filling volume will be considered first. To introduce a reproducible volume of liquid into the viscometer, the viscometer and the liquid must both be at some standard temperature (20°C for this work) each time the viscometer is charged. To obviate the inconvenience of this procedure, fillings are made at ambient temperature, which is observed, and an appropriate correction, Δh_t , is then calculated to account for

any difference between the filling at the observed temperature and a standard filling at a temperature of 20° C. The calculation of this correction is similar to that of Δh_2 , which follows.

A second factor affecting h , which gives rise to a correction Δh_2 , is the change in effective head with differences between the calibration temperature and that of subsequent runs. The calculation of this correction is based on the cubical expansion of the viscometer and test liquid, together with the mean diameter of the working part of reservoir C, figure 6, [8]. For the most precise work an accurate knowledge of the internal diameter of C is necessary. This measurement was made by plugging the lower end of the capillary with wax and then filling the bottom part of the viscometer with mercury to a low level in C. Weighed increments of mercury were added, and the resulting increases in level in C were measured with a depth gage, from which data a mean internal diameter was calculated.

From differences in the factor $(1 - \rho_a/\rho)$ between calibrating and operating conditions a Δh_3 is calculated. The density of the air in the viscometer is a function of the temperature and amount of water vapor present, neither of which is known accurately, but no serious errors are introduced by assuming the air to be 50-percent saturated and at the test temperature.

The factor most difficult to evaluate is the variation of the mean head with surface tension. In the work reported here, viscosity measurements of oils made in water-calibrated viscometers required the most careful estimates of the effects of surface tension. In the case of water, the contribution of surface effects to the effective head was determined experimentally and also calculated. The experimental determination was made with a glass bulb blown as nearly as possible to the size and shape of the fiducial bulb in the viscometer. The bulb was connected through a U-shaped tube to a cylindrical glass tube about 1 cm in diameter and held vertically close to the side of the bulb. The bulb and tube were then mounted in a small bath of oil having close to the same index of refraction as the bulb. Water was introduced into the tube until the level stood in the neck at the bottom of the bulb. The difference between the liquid levels in bulb and tube was then measured with a micrometer microscope mounted for vertical measurements. From this difference and a calculated value for the capillary rise in the cylindrical tube, the rise at this particular level in the bulb was obtained. The calculation of the rise in the cylindrical tube was made by using Sugden's table [9]. A known volume of water was then added and the measurements repeated. The portion of the added volume going into the bulb was the difference between the added volume and the volume increase in the tube as calculated from the change in level in the tube. This process was repeated, taking about 20 increments of volume to fill the bulb. From these data and a measured value of the head in the viscometer at a known level in the bulb, a value of

the mean head in an interval, h_i , was estimated for each of the 20 intervals. Then, knowing the volume, ΔV , and the capillary rise, h_r , for each interval, terms of the form $\Delta V h_r/h_i$ were calculated for each interval. The quotient

$$\frac{\sum \frac{\Delta V}{h_i} h_r}{\sum \frac{\Delta V}{h_i}}$$

then gave a time-weighted mean value for the capillary rise in the bulb as a whole. The rise in the cylindrical lower reservoir was calculated by using Sugden's table and subtracted from the mean value for the bulb to get a net effect for water in the viscometer. The same techniques were used to determine a net value of the surface tension for each of the oils tested. From the difference between water and oil, a correction, Δh_4 , was calculated for application to data obtained with oil.

The net surface tension effect for water in the viscometer was also obtained by calculation alone. For this purpose, a vertical section through the fiducial bulb was plotted on a large scale as accurately as possible. The bulb was then divided into 13 sections, and a value of $\Delta V h_r/h_i$ was calculated for each. With the aid of Bashforth and Adams' tables [10], each value of ΔV was calculated by using the geometry of the bulb as plotted and the calculated change in meniscus volume between the top and bottom of the section. The tables were also used in calculating h_r for each section. This method has been given in more detail by Barr [11]. The mean value for the bulb was obtained weighting each section with respect to time, as was done in the experimental method. The calculations yielded a value within 0.01 percent of the experimental result, which lent confidence to both methods. Because of limited range of Bashforth and Adams' tables, the calculation could not be made for the oils.

Thus far in the treatment of the factors affecting K in eq (7), it has been assumed that the volume of flow, V , is constant under all conditions. For application to the work reported here, the validity of this assumption was carefully tested. Bulbs similar in size and shape to the fiducial bulbs in the Cannon viscometers were blown with capillary stems about 1 cm long above and below the bulb. To detect differences in the volume of flow of water and the several oils from a bulb, a capillary was attached below the bulb with neoprene tubing so that the bulb could be quickly disconnected. The capillary bore was selected to give about the same time of flow for a particular liquid as was found in the Cannon viscometer. By weighing the test bulb empty and again after a liquid had been run from it at the rate controlled by the resistance of the capillary, the volume of liquid remaining on the walls of the bulb was obtained. From the difference between results obtained with

a calibrating liquid and a test liquid, a correction to K_c could be calculated. Only one instance of a correction as large as 0.01 percent was found, and this so-called drainage correction was applied.

The viscometer is filled by holding it in an inverted position with the end of the upper capillary immersed in the liquid under test. Liquid is drawn into the viscometer by applying suction to the other arm until the level reaches a position slightly beyond the mark F (fig. 6). Applying just enough suction to hold the liquid level at approximately this position, the upper capillary is lifted from the liquid and the operator's finger is placed over its end. With the instrument still inverted, excess liquid is carefully bled out of the capillary past the finger tip until the liquid level reaches F. The viscometer is then returned to its normal upright position, and the finger is removed with a gentle wiping action. In this manner a reproducible filling volume is introduced. After filling the viscometer it is mounted in its bath, and sufficient time is allowed for the fiducial bulb B to empty and for the sample to come to the bath temperature before starting a test. To make a determination, the liquid is pushed up under 17-mm-Hg air pressure until the upper meniscus stands about 5 mm above the mark at the top of bulb B. The air pressure is then released, and the time for bulb B to empty is observed. With relatively low viscosity oils, raising the liquid with vacuum at the start of a run sometimes results in a time of flow slightly higher than when air pressure is used. Such differences are attributed to the removal of air from the sample under reduced pressure. It is therefore considered better technique to use air pressure as any change in the amount of air dissolved in the oil will start at the surface farthest removed from the liquid passing through the capillary.

When the liquid is pushed up at the start of a run, the meniscus level in reservoir C is lowered, leaving some liquid behind on the walls. The amount of liquid left on the walls influences the level in C and hence the value of h . By always using the same pressure in pushing the liquid up, the level in C is lowered at a rate inversely proportional to the liquid viscosity, which leaves about the same amount of liquid on the walls for each test. Calculations indicate that this procedure eliminates significant variations in h .

3.2. Calibration and Results

The calibration of the Cannon viscometers consists in evaluating K_c and B in eq (9). To illustrate the method, eq (9) is rewritten

$$\frac{\eta}{\rho t_c} = K_c - \frac{B}{t_c^2} \quad (10)$$

in which t_c is substituted for t without detectable error. Liquids having different kinematic viscosities η/ρ are run in the viscometer, and values of $\eta/(\rho t_c)$ are plotted against $1/t_c^2$. Values of K_c and B are

then obtained from the resulting curve. As unpublished results in this and other laboratories have shown that B may not remain constant over the useful range of Reynolds numbers for this type of viscometer, the calibration must embrace the range in which the instrument is to be used. In practice, therefore, the calibration curve consists of a plot of $\eta/(\rho t_c)$ as a function of $1/t_c^2$ or R , and for a particular viscosity determination values of K_c and B are obtained from the curve at the appropriate value of $1/t_c^2$ or R .

The four Cannon viscometers used in this work are identified in table 3. Of these, M25-1 and M25-2 were calibrated with water, whereas M104 and M105 were calibrated subsequently with two hydrocarbon oils whose viscosities were determined in M25-1 and M25-2. The calibration data obtained with M25-1 and M25-2 are given in appendix 7.5, and from these data the calibration curves in figure 7 were plotted.

The curves were arbitrarily drawn through the values of $\eta/(\rho t_c)$ at Reynolds numbers of about 15, which were obtained with water at 20° C, because a value for the viscosity of water at 20° C was taken as the primary standard for calibration. The points at higher Reynolds numbers were obtained with water at 40°, 60°, and 80° C. The values used for the properties of water at these temperatures are given in appendix 7.6. As K_c refers to the conditions existent with water at 20° C, times of flow obtained at the higher temperatures were corrected by appropriate values of the factor $(1 + \Delta h/h)$ in eq (8).

It is evident that the value of B is zero ($m=0$) for these two viscometers up to a Reynolds number of at least 110. Because they were used at values of R never exceeding 50, the determinations made in these instruments were calculated by means of the equation

$$\frac{\eta}{\rho} = K_c t_c \quad (11)$$

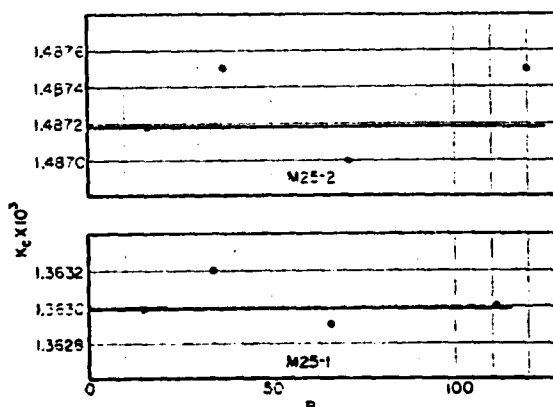


FIGURE 7. Calibration curves for Cannon viscometers numbers M25-1 and M25-2.

TABLE 3. Essential dimensions of Cannon viscometers

Viscometer	<i>l</i>	<i>r</i>	<i>V</i>	<i>A</i>	Filling volume	Radius of reservoir
	cm	cm	cm ³	cm	cm ³	cm
M25-1.....	44.5	0.0180	3.11	46.5	6.85	1.52
M25-2.....	44.5	.0165	3.13	46.3	6.77	1.50
M104.....	44.5	.0294	3.64	46.6	7.68	1.53
M105.....	44.5	.0285	3.54	46.6	7.53	1.55

Viscometers M104 and M105 were calibrated with oils A and B, using values of their viscosities as determined in M25-1 and M25-2. The calibration data are given in appendix 7.7. These viscometers were calibrated and used at $R < 10$, and hence it was assumed that $B=0$ and eq (11) was applicable. For consistency, the values of K_c for these viscometers were also calculated for the conditions that would exist with water, even though water was never run in these viscometers. The values of the viscosities of *n*-heptane and the three mineral oils, as determined in the Cannon viscometers, are given in table 4. Detailed calculations are given in appendix 7.8. In table 4, kinematic viscosities are converted to absolute units for comparison with the measurements made in the Bingham viscometers. The results obtained independently in the two types of viscometers are in good agreement, the largest discrepancy being 1 part in 2,000 in the case of *n*-heptane. As the techniques employed and the nature of the corrections applied are quite different with the two types of instruments, it is not likely that similar errors are involved in both methods. Hence, there is indication that the treatments of the data obtained in both types of viscometers are free of gross error.

TABLE 4. Results at 20° C with Cannon viscometers compared with Bingham results

Oil	Viscometer	η/ρ	η/ρ mean	ρ	η	η by Bingham
		cp	cp	g/cm ³	cp	cp
<i>n</i> -Heptane.....	M25-1	0.60070	0.60070	0.6841	0.4109	0.4111
Do.....	M25-2	.60069				
A.....	M25-1	2.4641	2.4643	.78110	1.9249	1.9250
A.....	M25-2	2.4645				
B.....	M25-1	9.1809	9.1812	.82907	7.612	7.610
B.....	M25-2	9.1815				
C.....	M104	49.583	49.584	.8637	42.63	42.52
C.....	M105	49.585				

4. Discussion of Results

4.1. Sources of Error in Using Bingham Viscometers

From a thorough examination of the various factors involved in the use of the Bingham viscometers, it appears that the greatest source of uncertainty arises from the unavoidable use of relatively low pressures in establishing the portion of the calibration curve corresponding to low Reynolds numbers. The lower pressures are more difficult to maintain

relatively steady and measure with a given relative precision, and larger errors are introduced for given uncertainties in the values of the head corrections. This point is illustrated from the data for viscometer number 1 by a comparison of run 1-24, made at a Reynolds number of 8.5, with run 1-38 made at $R=41$ (see appendix 7.1). For run 1-38, with an applied pressure of 73 mm Hg (100 cm H₂O), the level head correction is 0.07 percent, and the logarithmic head correction is 0.01 percent, whereas for run 1-24 with an applied pressure of 15 mm Hg (21 cm H₂O), the level head correction is 0.31 percent, and the logarithmic head correction is 0.24 percent. Thus in the necessary extension of the calibration curve from $R=41$ down to $R=8.5$, the sum of the head corrections is increased from 0.08 percent to 0.55 percent of the applied pressure. For each of the three Bingham viscometers used in this work the value of the level head was determined experimentally, as described previously, the accuracy of the determinations being limited chiefly by the precision with which the pressures could be measured. The experimental evaluation of the logarithmic head corrections with sufficient accuracy, however, was not found feasible, and hence, the corrections were calculated, use being made of an equation given by Barr [4], by which the mean effective pressure for a run is calculated from the known initial and final pressures. This equation was developed on the assumption that each bulb of the viscometer had the shape of two cones placed base-to-base. Although this simple geometry is not exactly realized in any of these viscometers, the correction is not very sensitive to instrument dimensions. Further confidence is lent to the calculations by the fact that good agreement is always found between viscosity measurements made first under conditions where the correction is relatively large and again when the correction is small. This is shown to some extent by the viscosity determinations made on oil A in viscometer 1 (see appendix 7.4). This oil was run first at a pressure of 20 mm Hg, with a logarithmic head correction of 0.08 percent, and then at a pressure of 237 mm Hg, where the correction is negligible. The agreement between these runs is very good, which indicates that the shape of the calibration curve, and the values of the head corrections applied are essentially correct.

It has been shown [12] that the viscosity of water is not significantly affected either by change in the amount of air in solution or by change in pressure under the conditions of these tests. Although the viscosities of the hydrocarbon liquids are more sensitive to these variables, the experimental conditions were chosen such that the variations in the dissolved air under the different test conditions would not be expected to have measurable effects. Furthermore, unpublished experiments at the Bureau have shown that the corrections as applied for the change of viscosity of these hydrocarbon liquids with pressure [2] are probably not in error by more than 30 percent. In the tests recorded in Appendix 7.4, the largest correction occurs with runs 5-17 and

5-18 on oil C, with an applied pressure of 595 mm Hg. As the pressure correction for these runs is 0.08 percent, an error of 30 percent in the correction will amount to only 0.02 percent in the viscosity determination.

4.2. Sources of Error in Using Cannon Viscometers

The first considerations are concerned with the establishment of the calibration curves given in figure 7 for the two viscometers calibrated with water. In the work reported here these viscometers were used at Reynolds numbers in the range 0.03 to 42, and hence only factors affecting this portion of each curve will influence the results. As the determinations in the viscometers were to give results based on a value for the viscosity of water at 20° C, each calibration curve was arbitrarily put through the point at a Reynolds number of about 15, which represents the data obtained at this temperature. At this point, uncertainties in the value of K_c , which is equal to $\eta/\rho t_c$, will depend only on errors in t_c , as the value of η is taken without error and ρ is known with high accuracy. With reference to appendix 7.5, it is seen that for the data at 20° C, t_c is obtained from the observed time of flow t , by applying only a relatively small correction for filling temperature. This correction is readily calculable and is not considered as a source of error. Of the factors affecting t , the effects of errors in temperature measurement, or of temperature variations, are probably small. Both the platinum resistance thermometer and the Mueller G-2 bridge used for measuring temperature were calibrated shortly before or after tests were made, so that no error larger than 0.001 deg C is expected in the measured temperatures. Observed temperature variations during the tests were 0.002 deg C or less, with the mean temperature closer than is indicated by this spread. It is probable that the actual bath temperatures were within 0.002 deg of 20° C, which is equivalent to an uncertainty of only 0.005 percent in the viscosity of water. Calculations² of the precision of the mean values of t as recorded in appendix 7.5 indicate an uncertainty in the mean time of flow for viscometer M25-1 of ± 0.03 percent and for viscometer M25-2 an uncertainty of ± 0.007 percent. These limits reflect errors due to variations in filling the viscometers, bath temperature, timing, and unrecognized factors. From the above considerations, the values of K_c at $R=15$ for the two viscometers are probably within ± 0.03 percent of their true values.

Having established one point on each calibration curve, the other important factor is the shape of the curves in the range $R < 50$. From theoretical considerations [3], with increasing values of R these curves should be horizontal lines until some value of R is exceeded and a gradually increasingly negative slope begins to develop. No known theory can account for a positive slope at these Reynolds num-

bers. The values of $\eta/\rho t_c$ for water at 40°, 60°, and 80° C were therefore obtained and plotted to indicate whether the curves could be assumed to have zero slope up to $R=50$. These values of $\eta/\rho t_c$ were computed by using the values of η/ρ given in appendix 7.5 and are believed to be accurate within 0.1 percent. It is seen that zero slope is indicated in the range of Reynolds numbers covered, and unreasonably large errors in the values of $\eta/\rho t_c$ for water at 40°, 60°, and 80° C would be required to change the positions of the calibration curves at $R < 50$ by as much as 0.01 percent.

The calculations of the viscosities of *n*-heptane and oils A and B from the data obtained with these two water-calibrated viscometers are recorded in appendix 7.8. These data show that the times of flow for repeat fillings of a given viscometer with a given oil are in even better agreement than was the case with repeat fillings with water. It is estimated that the mean times of flow for the two fillings with each oil should be within ± 0.01 percent of their true values, based upon 99-percent confidence limits.

In appendix 7.8 the values of t_c are obtained by applying at least three corrections to the observed times of flow. Of these, $\Delta h_1/h$ is calculated without significant error. With reference to section 3.1 it is seen that $\Delta h_2/h$ is dependent upon differences in ρ air/ ρ liquid between calibrating and test conditions. The values of $\Delta h_1/h$ were calculated by assuming the air in the viscometers to be 50-percent saturated under all conditions, which was not always the case. No significant error is introduced by this assumption, however, as the difference between the values of $\Delta h_1/h$, assuming dry air and again assuming saturation, affects t_c by only 2 parts in 100,000. The third correction, $\Delta h_3/h$, which is applied to account for the difference in head caused by the difference in surface tension between water and the oils, is perhaps the greatest source of uncertainty. As described previously, the calculated value of the effect of surface tension for water at 20° C was in good agreement with the experimental value, but both calculations and experiments were sufficiently complex as to make it difficult to estimate the accuracy of either. It is believed no error greater than ± 0.02 percent is introduced by this correction, but this can not be said with certainty.

The drainage factors recorded in appendix 7.8 based upon experiments described in section 3.1, are believed to be known to about 0.002 percent and are therefore not significantly in error. No satisfactory explanation has been found for the different behavior of oil A, as compared with *n*-heptane and the other two oils, in bulbs of similar shape and volume to the fiducial bulbs of viscometers M25-1 and M25-2 (see fig. 6). Oil A did not show this different behavior in a somewhat more elongated bulb similar to the fiducial bulbs of viscometers M104 and M105.

In the calibration of viscometers M104 and M105 with oils A and B and the subsequent determinations of the viscosity of oil C, the sources and magnitudes of error are essentially the same as described above for the oil runs in viscometers M25-1 and M25-2.

² The calculations were made by the American Society for Testing Materials' methods [18], assuming that the true value of the mean will be within the limits given 99 times in 100.

4.3. Heating Effects in Capillaries

So far in the treatment of the data it has been assumed that, once the liquid under test has reached the temperature of the bath in which the viscometer is immersed, it remains at this temperature during the measurement. Because heat is generated in the liquid as it is sheared in the capillary, it is obvious that this assumption cannot be strictly true. As the temperature will vary from point-to-point within the capillary, the viscosity will vary accordingly, and what is measured is a mean value of the viscosity corresponding to some effective mean value of the temperature within the capillary. In attempting to calculate this mean effective temperature, one is unable to postulate what conditions of temperature distribution and heat transfer exist for a given flow condition. Hersey [14] and Hersey and Zimmer [15] have derived equations for calculating the mean effective temperature rise, first assuming conditions of adiabatic flow and then for conditions of thermal equilibrium in the liquid flowing in the capillary. Corrections based on these equations have been calculated for the data in both the Bingham and Cannon viscometers. Referring to appendices 7.4 and 7.8 it is seen that oil C was run in a Bingham viscometer at pressures of 595 mm Hg (runs 5-17 and 5-18) and 303 mm Hg (runs 5-15 and 5-16), and also in Cannon viscometers at 29 mm Hg. If we should assume the conditions defined by Hersey and Zimmer as incomplete adiabatic flow and calculate corrections, using their eq (5) [15], we get a viscosity correction of +0.70 percent for the tests in the Bingham viscometer at 595 mm Hg, and a correction of +0.02 percent for the tests in the Cannon viscometers. On this basis the tests at 595 mm Hg uncorrected, should be about 0.7 percent lower than the runs at 29 mm Hg. As the results recorded in table 4 and appendix 7.4 are in good agreement at all three pressures without these corrections, it must be concluded that conditions of incomplete adiabatic flow are not approximated in these tests. Calculations based on Hersey's eq (13) [13], which assumes flow under the conditions of thermal equilibrium, yield negligibly small corrections, in agreement with the evidence of the tests referred to above.

It should be noted that the effects of heating in the capillary are not only probably negligibly small under the conditions of the tests reported here, but in addition, through the course of calibration and use of a viscometer, the effects tend to be minimized. In the calibration of an instrument, heating effects result in a negative correction to the calibration constant, while in a subsequent determination made in the viscometer the effects result in a positive correction to the time of flow. Thus, even though no corrections are applied, the product of the instrument constant and the time of flow tends to yield a correct result in the viscosity determination. Of course this will only be strictly true when the pressure drop through the capillary is the same for both the calibration and the determination, and when the liquid whose viscosity is being determined and the

calibrating liquid have the same heat capacity and temperature coefficient of viscosity. The pertinent physical properties of the liquids involved will usually be sufficiently alike, however, to minimize an accumulation of errors in the usual laboratory practice of calibrating a series of viscometers, graduated as to capillary diameter, by calibrating a larger capillary with an oil whose viscosity has been determined in a smaller one.

4.4. Variability of End Corrections With Reynolds Number

The possible existence of curvature in Pt versus R plots for viscometers of the Bingham type, such as shown in figures 2 and 3, has not been generally recognized. Most observers have confined their calibrations to the higher rates of flow in order to obtain more accurate pressure measurements, and in addition, there has often existed a disregard or inaccurate estimation of the level head and logarithmic head corrections, which may mask the true nature of the calibration curve at the lower Reynolds numbers. The curvature found in the plots for viscometers 1 and 20, however, is not inconsistent with the theory of end corrections and may be explained through a consideration of the nature of the coefficients m and n in eq (1).

The value of m is dependent upon the work done in accelerating the liquid from essential rest to the parabolic distribution of velocities existing after a sufficient entrance length has been traversed. This work is done not against viscous forces, but only imparts kinetic energy to the flowing liquid at the expense of the applied pressure. The value of n arises in part from the excess work done against viscous forces in the entrance length as compared with an equivalent length where the distribution of velocities is parabolic throughout. At sufficiently high Reynolds numbers the kinetic energy of the liquid streaming out of the exit end of the capillary is dissipated as heat [16] in the enlarged part of the viscometer past the capillary. For this condition, the phenomena at the exit end will make a negligible contribution to the values of m and n . At lower Reynolds numbers, however, part or all of the kinetic energy may be expended against viscous resistance close to the exit of the capillary. The value of m for a given Reynolds number will then depend upon the difference between the work done in acceleration at the entrance end and the amount of kinetic energy used in overcoming viscous resistance at the exit end. The magnitude of n will be the sum of the extra work done against viscous resistance at the two ends. It follows then that higher values of m correspond to lower values of n and conversely. Also, when m is constant over a range of Reynolds numbers, n should also be constant. Dorsey [5] has treated this subject at some length and concludes that, for capillaries with square-cut ends, m is zero, and n has a constant value of 1.14 up to a Reynolds number of 10, while at higher Reynolds numbers, $m=1$ and n has a constant value of 0.57. He

recognizes, however, that the values of m and n will be affected by the geometry of the entrance and exit ends of the bore. In the construction of the Bingham viscometers some glass blowing was done at the ends of the capillaries so that they are not precisely square-cut, but evidence slight fire polishing at the edge of the bore. With this geometry it is not surprising that these viscometers show an extended transition region (approximately $R=10$ to 60) between the range where $m=0$ and the range above $R=60$ where m becomes constant.

For Bingham viscometer 1 the constant value of m is 1.12, which is in agreement with values reported by others for capillaries with squarecut ends [3]. The lower value of $m=0.95$ found for Bingham No. 20, may be the result of some peculiarity in the shape of the ends of the capillary bore as a result of glass blowing. With the Cannon viscometers M25-1 and M25-2, it was found that $m=0$ up to at least a Reynolds number of 120, which is as high as the calibration was carried. This condition is undoubtedly associated with the gradual tapers through which the bores of these capillaries expand. It is probable that at sufficiently higher rates of flow these calibration curves would also pass through a transition region and then assume a constant slope corresponding to a value of m which is close to one.

5. Conclusion

In making the measurements reported here, every reasonable precaution was taken so that the results would reflect the accuracy of which each viscometric method was capable. The viscosity values of the four liquids as determined independently by the two methods were in better agreement than was anticipated, and hence it is believed that both methods are relatively free of error. Reviewing the techniques and sources of error critically, however, it is apparent that the necessary steps in calibrating the Bingham viscometers are more complicated and contain more possibilities of uncertainty than are present in calibrating the Cannon viscometers. The experimental difficulties in establishing

the calibration curve with water at low Reynolds numbers and the uncertain effects of heating in the capillary are perhaps the weakest points in the method. On the other hand, the relative simplicity of the method with the Cannon viscometers makes this method singularly attractive and inherently more accurate. The greatest difficulty with this method seems to lie in adequately correcting the head for the difference in the surface tensions of water and oil. The procedures described here for evaluating this correction are cumbersome and time consuming to the extent that less accurate estimates of the correction are resorted to in most laboratories. It is possible that a redesign of the shape of the fiducial bulb of the viscometer would simplify the evaluation of this correction. For example, a cylindrical bulb with a conical top and bottom would present simple geometric shapes for which surface tension effects are readily calculable by Barr's method [11]. Any redesign of this nature, however, would have to be accompanied by considerations of the drainage characteristics of the bulb as well.

6. References

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